

# THE ABSORPTION OF NEAR INFRA-RED RADIATION BY WATER-VAPOR

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# THE ABSORPTION OF NEAR INFRA-RED RADIATION BY WATER-VAPOR

BY W. W. SLEATOR

## I. INTRODUCTION

The study of the absorption of radiation in the atmosphere was begun by Langley,<sup>1</sup> whose bolographs, or maps of the sun's spectrum, show wide bands attributed by him to water-vapor. Paschen,<sup>2</sup> in work on the emission of radiation by gases, has investigated as well the absorption occurring in steam, and records in particular the effect of changes in temperature upon the wave-lengths of the radiation absorbed. His work has been extended by Eva von Bahr,<sup>3</sup> who has shown that the doublet between wave-lengths 5 and 7  $\mu$  is in reality very complex and contains about forty separate absorption bands arranged with some appearance of symmetry on either side of the wave-length 6.26  $\mu$ .

The combination principle suggested by Bjerrum,<sup>4</sup> in connection with his application to the case of molecular rotation of the quantum theory, is a fruitful hypothesis in the explanation of near infra-red absorption. Bjerrum's ideas have in fact been applied by Eucken<sup>5</sup> to the system of water bands presented in the work of Eva von Bahr, and that system seems to be accounted for in terms of two series of rotation-frequencies corresponding to two principal moments of inertia in the water molecule. More recent work by Rubens and Hettner<sup>6</sup> shows some evidence for the presence in the farther infra-red of a third series of rotation-frequencies. The

<sup>1</sup> *Resarches on Solar Heat* (Professional Papers of the Signal Service, No. 15, United States War Department).

<sup>2</sup> *Annalen der Physik*, **51**, 4, 1894; **52**, 210, 1894; **53**, 234, 1894.

<sup>3</sup> *Phil. Mag.*, **28**, 71, 1914; *Verhandlungen der deutschen Physikalischen Gesellschaft*, **15**, 731, 1913.

<sup>4</sup> *Nernst Festschrift*, p. 90.

<sup>5</sup> *Verhandlungen der deutschen Physikalischen Gesellschaft*, **15**, 1159, 1913; *Phil. Mag.*, **28**, 71, 1914.

<sup>6</sup> *Chemical Abstracts*, **11**, 1357, 1917; *Science Abstracts*, No. 234, p. 223, June 1917.

question of molecular structure is now intimately connected with the investigation of radiation, as is shown by further work of Bjerrum,<sup>1</sup> and important tests of the quantum hypothesis await experimental advances in the same field.<sup>2</sup>

The present paper gives an account of work undertaken to extend our knowledge of atmospheric absorption. It concerns particularly the region of the spectrum between the wave-lengths  $1.3$  and  $3 \mu$  and presents a detailed study of the absorption regions marked  $\Psi$ ,  $\Omega$ , and  $X$  on Langley's charts.

## II. APPARATUS

The work of Eva von Bahr was done with a prism spectrometer and radiomicrometer. In the work recounted here a higher dispersion was secured by the use of gratings, and the uncertainty of wave-lengths determined with the aid of a dispersion-curve was at the same time avoided. The troublesome overlapping of grating spectra has been eliminated by the use of a supplementary prism. The general arrangement is shown in Fig. 1. The apparatus takes the form of two spectrometers, each with fixed arm and single mirror.<sup>3</sup> By a proper setting of the prism a definite and limited portion of the spectrum is presented to the grating spectrometer. The prism serves in fact as an effective screen or filter.

A linear thermopile, incased at  $T$  in Fig. 1, and a galvanometer of the Paschen type constituted the detecting system. The ballistic deflections of the galvanometer observed on opening or closing the shutter at  $O$  serve to map out the spectrum of the Nernst glower used as the source of energy. The construction of the galvanometer was the first work done on the present problem.

The entire path of the light, shown in Fig. 1 by the dotted lines, is inclosed in a black box of double cardboard. It is of course not possible to make such a box tight, nor to get the air in it absolutely dry. In the section around the glower, however, the air could be saturated. Also energy-curves were plotted from data secured on winter nights, when cold air from out of doors was pumped through

<sup>1</sup> *Verhandlungen der deutschen Physikalischen Gesellschaft*, **16**, 737, 1914.

<sup>2</sup> *Ibid.*, **16**, 614, 1914; **15**, 1159, 1913.

<sup>3</sup> *Annalen der Physik*, **33**, 739, 1910.

sulphuric acid and phosphorus pentoxide into the cases. Sufficient difference appeared between the depths of the bands to enable us to attribute the absorption to water-vapor.

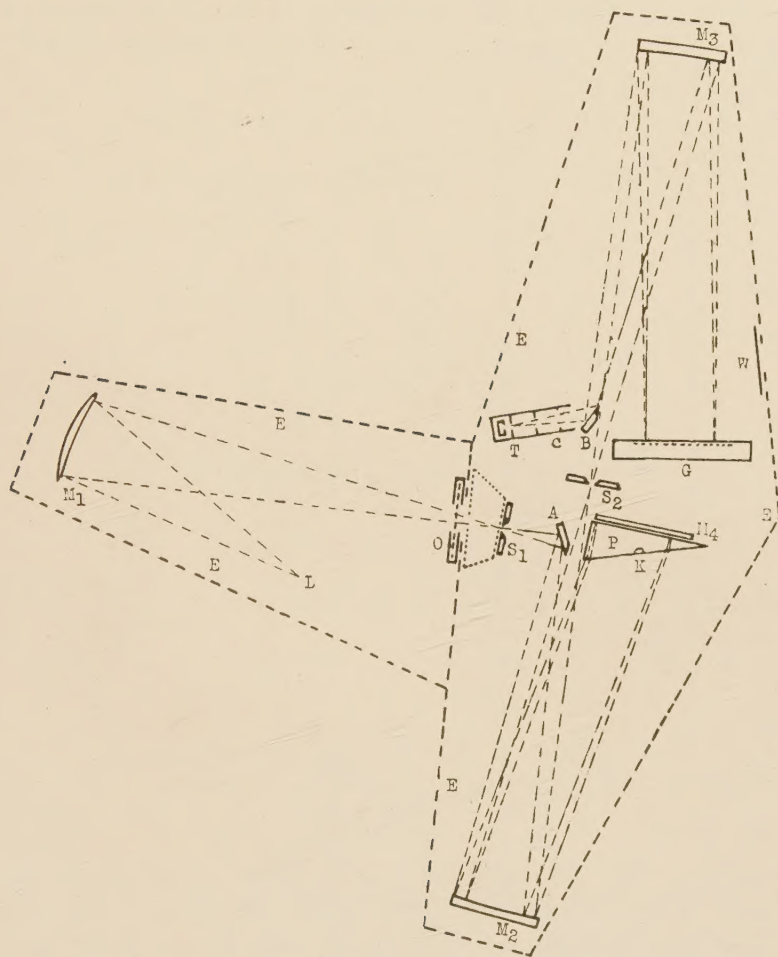


FIG. 1.—The spectrometer, scale 1 to 5

*L*, Nernst glower; *S*<sub>1</sub>, *S*<sub>2</sub>, slits; *M*<sub>1</sub>, 10 cm mirror, *f*=20 cm; *P*, salt prism; *M*<sub>2</sub>, *M*<sub>3</sub>, 10 cm mirrors, *f*=50 cm; *M*<sub>4</sub>, *A*, *B*, plane mirrors; *G*, grating; *C*, case for *T*, the thermopile; *W*, window in box *E*; *O*, shutter. The path of the light is *LM*<sub>1</sub>*S*<sub>1</sub>*A**M*<sub>2</sub>*P**M*<sub>4</sub>*P**M*<sub>3</sub>*S*<sub>2</sub>*M*<sub>3</sub>*G**M*<sub>3</sub>*B**T*. A spectrum appears at *S*<sub>2</sub>. *P* and *M*<sub>4</sub> rotate together about *K*, so that any region of the spectrum may be isolated for the grating, and the overlapping of spectra is avoided.



In the region of the spectrum near the wave-length  $2.6 \mu$  some work has been done with steam. The absorption took place in a chamber 15 cm long, which was kept hot by resistance coils, and could be swung into or out of the beam of light. The glass ends of the chamber were compensated for by two pieces cut from the same

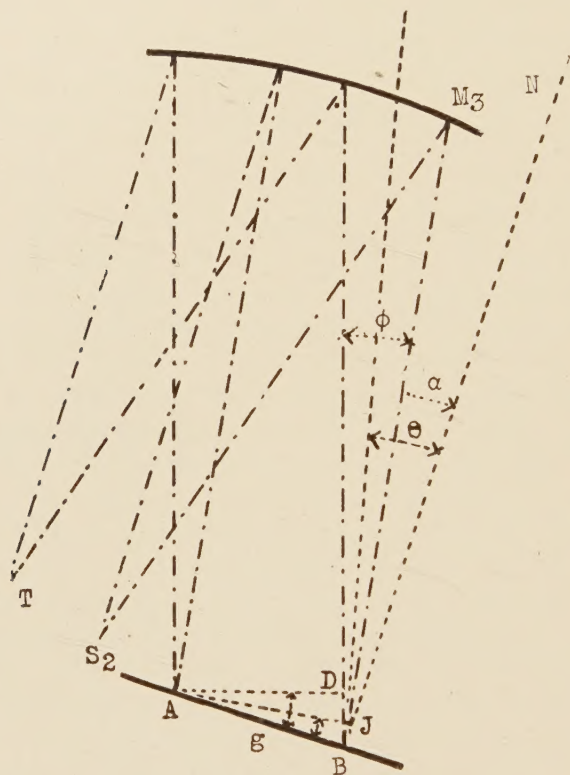


FIG. 2.—The spectrometer constant  $\kappa$  in the equation  $\lambda = \kappa \sin \theta$

$AB$  is the grating space,  $g$ . Light from  $S_2$  is sent to  $T$ .  $T$ ,  $S_2$ , and  $M_3$ , the mirror, are fixed, and rotation of the grating leaves  $\phi$  unchanged. The wave-length at  $T$  is determined by the relation  $n\lambda = DB + BJ$

$$\begin{aligned} &= g \sin (\alpha + \phi) + g \sin \alpha \\ &= 2g \sin \left( \alpha + \frac{1}{2}\phi \right) \cos \frac{1}{2}\phi \\ &= 2g \cos \frac{1}{2}\phi \sin \theta \\ &= \kappa \sin \theta \end{aligned}$$

$\theta = \frac{1}{2} (R_1 - R_2)$ ,  $R_1$  and  $R_2$  being circle readings on the two spectra of one order.

sheet of glass, through which the radiation passed when the steam chamber was drawn aside.

Three gratings have been employed in the course of the work. The smallest has a ruled surface 5 cm wide and about 2400 lines to the inch, and is referred to as the brass grating. The other two have effective surfaces 12.2 cm wide, are ruled on speculum metal, and are referred to as the 7500-line grating and the 15,000-line

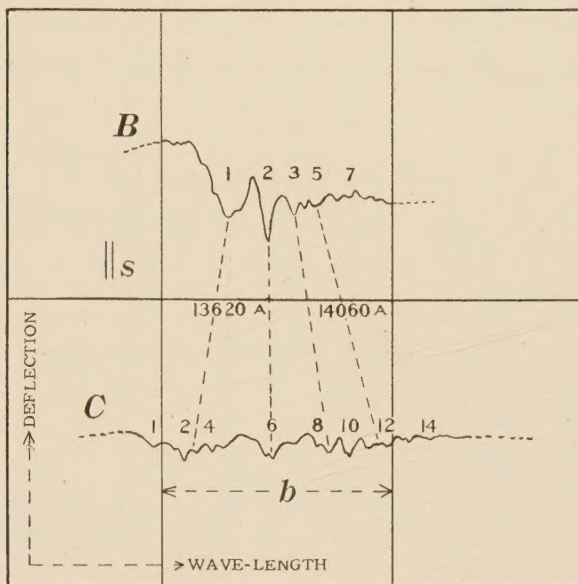


FIG. 3.—Energy-curves, region of  $1.3 \mu$ . The slit corresponds to 33 Å in *B* and 15 Å in *C*.

grating, the figures giving the number of lines per inch. In Figs. 3, 4, 5, and 6 the letters *A*, *B*, and *C* refer respectively to these gratings. They are mounted on the table of a Schmidt and Haensch spectrometer whose circle may be read to ten seconds.

Fig. 2 serves to illustrate the meaning and derivation of the equation

$$\lambda = \kappa \sin \theta,$$

used in computing wave-lengths from data secured with the fixed-arm spectrometer. To obtain the wave-length interval included at

one time in the slit of the thermopile, one considers first the resolving power of the grating. If the source  $S_2$  were very narrow, the width of the central bright band in the diffraction pattern produced by monochromatic light would be given by

$$w = \frac{2\lambda}{b \cos \theta} \cdot 500,$$

where  $b$  is the width of the grating in mm,  $\theta$  the angle by which the grating is turned from the normal, and 500 the focal length of the

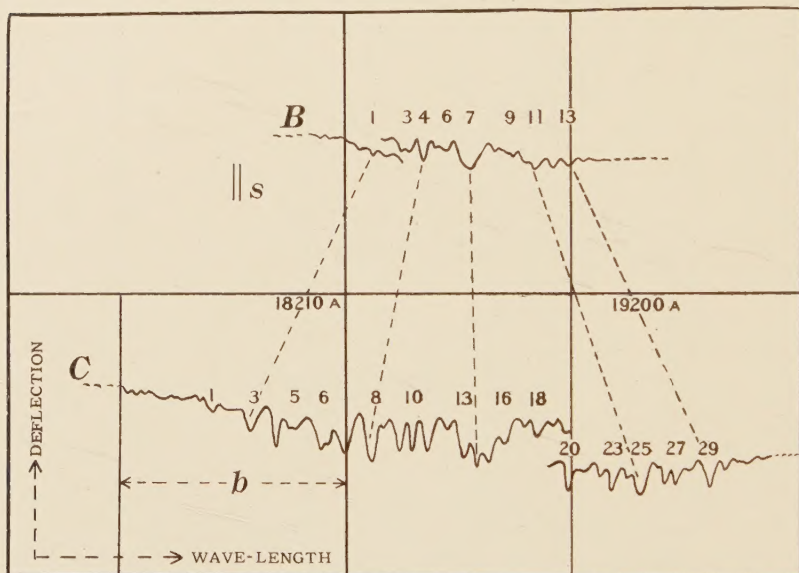


FIG. 4.—Energy-curves, region of  $1.8 \mu$ . The slit corresponds to  $33 \text{ Å}$  in  $B$  and  $14 \text{ Å}$  in  $C$ .

mirror in mm. For the 15,000-line grating  $w$  is  $0.03 \text{ mm}$  at  $2.6 \mu$ , and for the brass grating  $0.14 \text{ mm}$  at  $6 \mu$ . The slit  $S_2$  is  $\frac{1}{2} \text{ mm}$  wide, and its image in the plane of the slit of the thermopile is in the first case about  $0.52 \text{ mm}$  and in the second about  $0.57 \text{ mm}$  wide. With the slits now in use no great improvement in the purity of the spectrum can be attained by enlarging the grating.

The range of spectrum included in the slit is taken as the interval in wave-lengths between two beams whose centers are  $\frac{1}{2} \text{ mm}$  apart



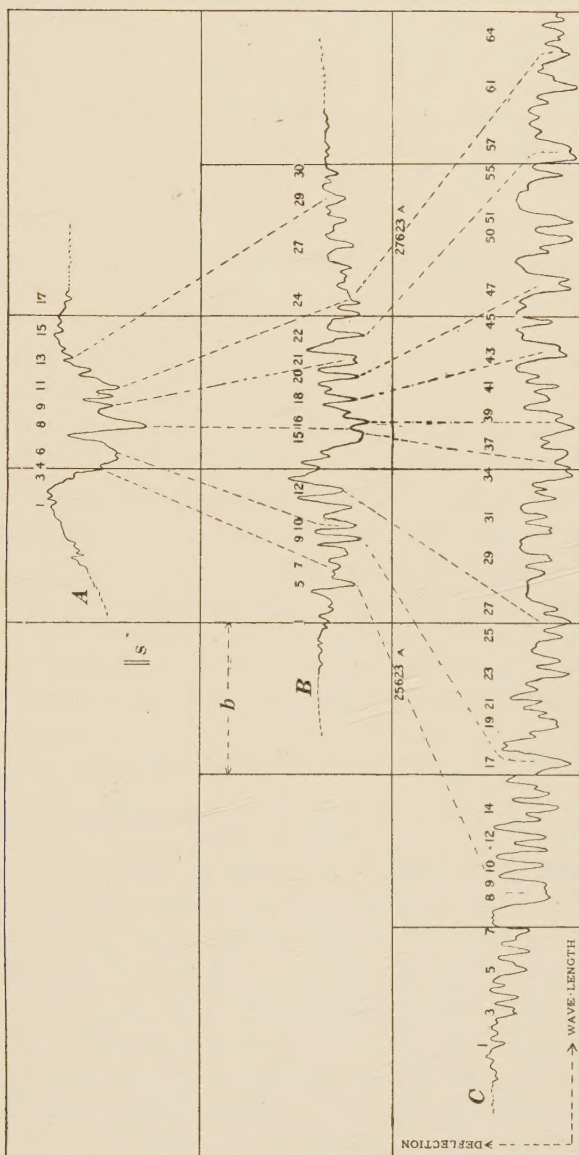


FIG. 5.—Energy-curves, region of  $2.6 \mu$ . The slit corresponds to  $105 \text{ A}$  in  $A$ , to  $31 \text{ A}$  in  $B$ , and to  $11 \text{ A}$  in  $C$ .  $C$  does not give the entire curve of this region as explored with the  $15,000$ -line grating.

in the plane of the thermopile. That slit does not take in the total energy even of a single wave-length, but does receive about three-fourths of the energy in the interval named. This interval corresponds to a variation in  $\phi$  (in Fig. 2) of  $\frac{1/2}{500}$  or 0.001 radian. Taking the equation for wave-length as

$$\lambda = 2g \cos \phi/2 \sin (a + \phi/2),$$

and considering that  $\phi/2$  is found by measurement to be  $1^\circ 16'$ , we have by differentiation the approximation

$$\begin{aligned} d\lambda &= K \cos \theta d\theta \\ &= K \cos \theta \frac{d\phi}{2}. \end{aligned}$$

This expression gives the values set down with the figures, which are a little too large. In order to throw a single beam from one

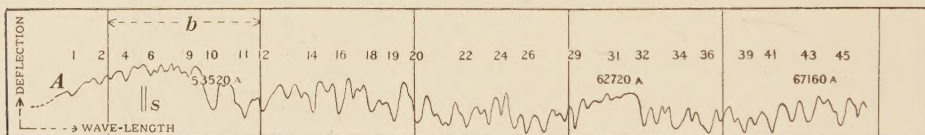


FIG. 6.—Energy-curve, part of the region of  $6 \mu$ . The slit corresponds to  $100 \text{ \AA}$

side of the slit of the thermopile to the other,  $\phi$  must be changed by  $\frac{1/2}{500}$  or 0.001 radian, as above, and this demands a change in  $a$  of 0.0005 radian and a corresponding motion of the grating. 0.0005 radian is  $1'7$ , and the spectrum interval may be checked by noting the value of  $1'7$  in units of wave-length along an energy-curve. At  $2.6 \mu$  the 15,000-line grating gives this interval as  $10.4 \text{ \AA}$ .

The green line of the spectrum of mercury ( $\lambda = 5460.74 \text{ \AA}$ , Kaye and Laby's tables) was used for visual calibration, the bright line and the slit of the thermopile being viewed objectively. In the case of the brass grating no visible lines could be observed, but the actual grating-space was known, and

$$K = 2g \cos \frac{1}{2}\phi$$

was computed from data obtained from measurement.



## III. THE CURVES

Figs. 3, 4, 5, and 6 present a summary of the experimental work. Except in Fig. 6 each energy-curve is one of three secured, for two of them the air being saturated and for one dried. The bands are numbered arbitrarily for reference to the tables. The letters *A*, *B*, and *C* refer respectively to the brass, the 7500-line, and the 15,000-line grating. In Fig. 7, as well as in the others, the distance *b* denotes  $1^\circ$  on the circle and *s* shows the relative size of the thermopile slit.

Fig. 7 represents part of the region at  $2.6\ \mu$  as mapped with the 7500-line grating. The upper curve (lettered *D*) does not show the galvanometer deflections but gives the percentage of incident energy transmitted by steam. The effect of drying the air appears also in this figure, in curve *E*, and it will be noted that the curve for steam accentuates the peculiarities of *F*, the "air-saturated" curve, peculiarities which the curve secured with dried air decidedly obscures. It seems that the temperature of the absorbing vapor has no effect on the position of an individual band. According to Paschen's work, already cited, we conclude that the relative intensities of the bands must change, so that those that are deepest at one temperature are not deepest at another. But the present work cannot confirm nor deny this effect. The effect on the absorption of drying the air, shown in Fig. 7, was found even more definitely with the finer grating, at  $1.3$  and  $1.8\ \mu$ , as well as at  $2.6\ \mu$ . All the deeper bands are less marked when the air is dry. This does not appear so clearly with the shallow bands, but it may be that in the "air-saturated" curves the presence of weak bands is masked by their more prominent neighbors. It is upon such evidence as appears in Fig. 7 that we ascribe the absorption to water-vapor.

With the 7500-line grating the intervals of the spectrum between the absorption bands at  $1.3$  and  $1.8\ \mu$ , and between those at  $1.8$  and  $2.6\ \mu$ , were carefully explored and were found to present no evidence of atmospheric absorption.

In Figs. 3 and 5 the upper curves are decidedly similar. This similarity suggests that one of these absorption regions may be a harmonic of the other in the sense suggested by Kemble.<sup>1</sup> However,

<sup>1</sup> *Physical Review*, **8**, 689, 1916.

a frequency half that corresponding to band No. 2 in Fig. 3 corresponds nearly to band No. 11 in Fig. 5 rather than to band

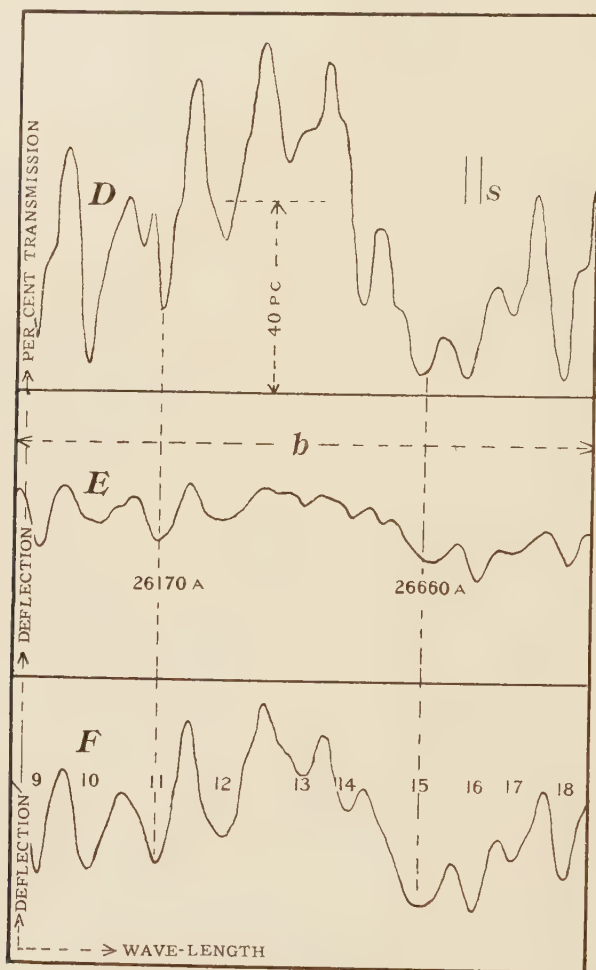


FIG. 7.—Part of the region of  $2.6\ \mu$ , 7500-line grating. *D* gives the percentage of energy transmitted by steam at  $110$  to  $120^\circ\text{C}$ . and 1 atmosphere pressure. *E* is an energy-curve with the air partly dried, *F* an energy-curve with the air saturated at about  $35^\circ\text{C}$ .

No. 8, and the same lack of agreement appears in the lower curves. Evidently the simple idea of harmonics does not apply.



A comparison of the energy-curves in Fig. 5, secured respectively with the 7500- and 15,000-line gratings, shows how the increased dispersion adds to our knowledge of the absorption. Bands No. 8 and No. 9 in the lower curve, for example, appear in the middle one as No. 5, a connection indicated in typical cases by the dotted lines, and appearing more definitely in the tables. These curves must be considered in any numerical computations made with absorption frequencies, for in the curves appear the individualities of the bands, which cannot well be expressed in numbers. In all cases the grating was turned  $1'$  for each new setting. At 6 and at  $2.6\ \mu$  six deflections were taken at each minute, and at  $1.3$  and  $1.8\ \mu$  four. The computations are based on curves which, for the region at  $2.6\ \mu$ , are about six feet long.

#### IV. THE TABLES

On pages 137 to 142 are set forth the wave-lengths and frequencies of the bands, which are denoted by the numbers given with the curves. Corresponding wave-lengths appear opposite each other. The gratings have been calibrated independently, the values given have been calculated from independent curves, and the agreement between opposite numbers is in general satisfactory. In connection with the region of  $6\ \mu$  is set forth some evidence of the symmetry demanded by Eucken's explanation, but unfortunately the work was not carried far enough to give this evidence much value. Some idea of the accuracy of the determinations of  $\lambda$  and  $N$  might be obtained by estimating the effects of various sources of error. But first one may consider the different values secured for the same quantity from the three corresponding curves. The "typical computations of  $\lambda$  and  $N$ " show these numbers for certain bands in the region at  $2.6\ \mu$ —bands taken quite at random. Considering the uncertainty in the value of  $K$  we should perhaps affect the wave-length by the probable error of  $\pm 2\ \text{\AA}$ . Errors in the circle of the spectrometer are probably negligible, especially since the calibration involved the same sections of the circle as were employed in the measurements. At  $6\ \mu$ , where we have only one curve, obtained under less favorable circumstances, we should perhaps write the wave-lengths with an error  $\pm 20\ \text{\AA}$ . A question mark in the tables

## TYPICAL DATA

The settings of the grating circle, and corresponding deflections of the galvanometer.

2 A.M., March 22, 1917. Grating temperature, 27°. Period of galvanometer, 6 secs.; E.M.F. applied to glower, 238 volts.

| Circle             | Deflections in mm  | Circle             | Deflections in mm   |
|--------------------|--------------------|--------------------|---------------------|
| 121° 10' . . . . . | 28-9- 9-8-9-9=28.7 | 120° 58' . . . . . | 18- 9- 8-9-9-9=18.7 |
| 0' . . . . .       | 26-7- 7-6-7-6=26.5 | 57' . . . . .      | 19-20- 0-0-0-0=19.8 |
| 8' . . . . .       | 23-2- 1-2-2-2=22.0 | 56' . . . . .      | 16- 7- 8-8-8-7=17.3 |
| 7' . . . . .       | 12-5- 6-6-4-5=14.7 | 55' . . . . .      | 9-11-10-1-0-1=10.3  |
| 6' . . . . .       | 11-2- 3-2-3-1=12.0 | 54' . . . . .      | 10- 0- 1-0-1-1=10.5 |
| 5' . . . . .       | 10-2- 2-1-2-2=11.5 | 53' . . . . .      | 18-22- 0-1-0-1=20.3 |
| 4' . . . . .       | 15-8- 7-7-8-7=17.0 | 52' . . . . .      | 24- 6- 5-5-6-5=25.2 |
| 3' . . . . .       | 17-6- 6-7-6-7=16.5 | 51' . . . . .      | 27- 7- 6-7-7-7=26.8 |
| 2' . . . . .       | 9-8-10-9-9-8= 8.8  | 50' . . . . .      | 27- 8- 6-7-6-8=27.0 |
| 1' . . . . .       | 5-5- 4-5-5-6= 5.0  | 49' . . . . .      | 25- 7- 6-8-6-7=26.5 |
| 121° 0' . . . . .  | 6-6- 5-6-6-6= 5.8  | 48' . . . . .      | 23- 6- 4-6-4-6=24.8 |
| 120° 59' . . . . . | 14-3- 4-3-4-3=13.5 | 47' . . . . .      | 22- 3- 1-4-2-3=22.5 |

## TYPICAL COMPUTATIONS OF WAVE-LENGTH AND FREQUENCY

REGION OF 2.6  $\mu$ 

| Band No.     | Curve No. | $\lambda$ | Mean $\lambda$ | $N$    | Mean $N$ |
|--------------|-----------|-----------|----------------|--------|----------|
| 20 . . . . . | { 1       | 26063.4   | 26066.2        | 383.69 | 383.64   |
|              | { 2       | 26068.8   |                | 383.60 |          |
|              | { 3       | 26066.5   |                | 383.63 |          |
| 23 . . . . . | { 1       | 26162.7   | 26161.6        | 382.22 | 382.24   |
|              | { 2       | 26161.7   |                | 382.25 |          |
|              | { 3       | 26160.4   |                | 382.26 |          |
| 27 . . . . . | { 1       | 26321.3   | 26325.5        | 379.92 | 379.86   |
|              | { 2       | 26330.0   |                | 379.79 |          |
|              | { 3       | 26325.3   |                | 379.86 |          |
| 31 . . . . . | { 1       | 26543.7   | 26546.4        | 376.74 | 376.70   |
|              | { 1'      | 26546.9   |                | 376.70 |          |
|              | { 2       | 26549.3   |                | 376.66 |          |
|              | { 3       | 26545.7   |                | 376.71 |          |
| 32 . . . . . | { 1       | 26587.4   | 26589.8        | 376.12 | 376.08   |
|              | { 1'      | 26589.5   |                | 376.09 |          |
|              | { 2       | 26590.9   |                | 376.07 |          |
|              | { 3       | 26591.4   |                | 376.06 |          |
| 33 . . . . . | { 1       | 26608.7   | 26609.9        | 375.82 | 375.80   |
|              | { 1'      | 26610.9   |                | 375.79 |          |
|              | { 2       | 26610.2   |                | 375.80 |          |
|              | { 3       | 26609.7   |                | 375.80 |          |

denotes not a doubtful band but a doubtful correspondence. The second column in the tables for the region at  $2.6\ \mu$  gives the relative depths of the bands as an indication of their importance in other infra-red work. A band numbered 1 seems to represent an absorption of less than 10 per cent, while 5 shows that perhaps 80 per cent of the incident energy is absorbed.

WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS  
OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM

REGION OF  $1.38\ \mu$

| 15,000-LINE GRATING |                   |                 | 7500-LINE GRATING |                   |                 |
|---------------------|-------------------|-----------------|-------------------|-------------------|-----------------|
| Band No.            | Wave-Length $\mu$ | Wave No. per mm | Band No.          | Wave-Length $\mu$ | Wave No. per mm |
| 1.....              | 13545             | 738.3           |                   |                   |                 |
| 2.....              | 13614             | 734.5           | 1                 | 13620             | 734             |
| 3.....              | 13643             | 733.0           |                   |                   |                 |
| 4.....              | 13678             | 731.1           |                   |                   |                 |
| 5.....              | 13710             | 729.4           |                   |                   |                 |
| 6.....              | 13820             | 723.6           | 2                 | 13820             | 723.5           |
| 7.....              | 13876             | 720.7           |                   |                   |                 |
| 8.....              | 13922             | 718.3           |                   |                   |                 |
| 9.....              | 13954             | 716.7           | 3                 | 13950             | 717             |
| 10.....             | 14000             | 714.3           | 4                 | 14010             | 714             |
| 11.....             | 14046             | 712.0           | 5                 | 14060             | 711             |
| 12.....             | 14092             | 709.7           |                   |                   |                 |
| 13.....             | 14140             | 707.2           |                   |                   |                 |
| 14.....             | 14186             | 704.9           | 6                 | 14170             | 706             |
|                     |                   |                 | 7                 | 14240             | 702             |



WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS  
OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM—*Continued*

REGION OF  $1.87\ \mu$

| 15,000-LINE GRATING |                          |                    | 7,500-LINE GRATING |                          |                    |
|---------------------|--------------------------|--------------------|--------------------|--------------------------|--------------------|
| Band No.            | Wave-Length $\text{\AA}$ | Wave No.<br>per mm | Band No.           | Wave-Length $\text{\AA}$ | Wave No.<br>per mm |
| 1.....              | 18110                    | 552.2              |                    |                          |                    |
| 2.....              | 18152                    | 550.9              |                    |                          |                    |
| 3.....              | 18202                    | 549.4              | 1                  | 18210                    | 549.1              |
| 4.....              | 18263                    | 547.6              |                    |                          |                    |
|                     |                          |                    | 2                  | 18287                    | 546.8              |
| 5.....              | 18306                    | 546.3              |                    |                          |                    |
| 6.....              | 18363                    | 544.6              |                    |                          |                    |
|                     |                          |                    | 3                  | 18398                    | 543.6              |
| 7.....              | 18414                    | 543.1              |                    |                          |                    |
| 8.....              | 18471                    | 541.4              | 4                  | 18467                    | 541.5              |
| 9.....              | 18534                    | 539.6              | 5                  | 18530                    | 539.7              |
| 10.....             | 18504                    | 538.7              |                    |                          |                    |
| 11.....             | 18595                    | 537.8              | 6                  | 18590                    | 537.9              |
| 12.....             | 18641                    | 536.4              |                    |                          |                    |
|                     |                          |                    |                    |                          |                    |
| 13.....             | 18676                    | 535.5              |                    |                          |                    |
| 14.....             | 18705                    | 534.6              | 7                  | 18704                    | 534.6              |
| 15.....             | 18729                    | 533.9              |                    |                          |                    |
|                     |                          |                    |                    |                          |                    |
| 16.....             | 18765                    | 532.9              |                    |                          |                    |
|                     |                          |                    |                    |                          |                    |
| 17.....             | 18806                    | 531.8              |                    |                          |                    |
| 18.....             | 18836                    | 530.9              | 8                  | 18836                    | 530.9              |
| 19.....             | 18862                    | 530.2              |                    |                          |                    |
|                     |                          |                    |                    |                          |                    |
| 20.....             | 18897                    | 529.2              |                    |                          |                    |
| 21.....             | 18926                    | 528.4              | 9                  | 18912                    | 528.8              |
|                     |                          |                    |                    |                          |                    |
| 22.....             | 18968                    | 527.2              |                    |                          |                    |
|                     |                          |                    |                    |                          |                    |
| 23.....             | 18995                    | 526.5              | 10                 | 18987                    | 526.7              |
|                     |                          |                    |                    |                          |                    |
| 24.....             | 19022                    | 525.7              |                    |                          |                    |
| 25.....             | 19054                    | 524.8              | 11                 | 19038                    | 525.3              |
|                     |                          |                    |                    |                          |                    |
| 26.....             | 19106                    | 523.4              |                    |                          |                    |
|                     |                          |                    |                    |                          |                    |
| 27.....             | 19133                    | 522.7              | 12                 | 19126                    | 522.9              |
| 28.....             | 19157                    | 522.0              |                    |                          |                    |
|                     |                          |                    |                    |                          |                    |
| 29.....             | 19199                    | 520.9              | 13                 | 19195                    | 521.0              |
|                     |                          |                    |                    |                          |                    |
| 30.....             | 19234                    | 519.9              | 14                 | 19264                    | 519.1              |

WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS  
OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM—*Continued*REGION OF  $2.6\ \mu$ 

| 15,000-LINE GRATING    |                    |               |                 | 7500-LINE GRATING |               |                 | HILGER BRASS GRATING |               |                 |
|------------------------|--------------------|---------------|-----------------|-------------------|---------------|-----------------|----------------------|---------------|-----------------|
| Band No.               | Relative Intensity | Wave-Length A | Wave No. per mm | Band No.          | Wave-Length A | Wave No. per mm | Band No.             | Wave-Length A | Wave No. per mm |
| 1.....                 | 1                  | 25235         | 396.28          |                   |               |                 | ?1                   | 24850         | 402.2           |
| 2.....                 | 1                  | 25262         | 395.85          |                   |               |                 | ?2                   | 25040         | 399.4           |
| 3.....                 | 2                  | 25311         | 395.09          |                   |               |                 |                      |               |                 |
| 4.....                 | 2                  | 25352         | 394.45          | 1                 | 25347         | 394.52          |                      |               |                 |
| 5.....                 | 2                  | 25425         | 393.31          | 2                 | 25432         | 393.21          |                      |               |                 |
| 6.....                 | 2                  | 25469         | 392.63          | ?3                | 25481         | 392.45          | ?3                   | 25490         | 392.2           |
| 7.....                 | 2                  | 25520         | 391.85          | 4                 | 25517         | 391.90          |                      |               |                 |
| 8.....                 | 3                  | 25608         | 390.50          |                   |               |                 |                      |               |                 |
|                        |                    |               |                 | 5                 | 25623         | 390.27          |                      |               |                 |
| 9.....                 | 3                  | 25636         | 390.08          |                   |               |                 |                      |               |                 |
| 10.....                | 3                  | 25688         | 389.29          | 6                 | 25696         | 389.17          |                      |               |                 |
| 11.....                | 3                  | 25727         | 388.70          |                   |               |                 |                      |               |                 |
|                        |                    |               |                 | 7                 | 25747         | 388.39          |                      |               |                 |
| 12.....                | 3                  | 25760         | 388.20          |                   |               |                 |                      |               |                 |
| 13.....                | 2                  | 25803         | 387.55          |                   |               |                 | 4                    | 25760         | 388.2           |
| 14.....                | 4                  | 25830         | 387.15          |                   |               |                 |                      |               |                 |
| 15.....                | 3                  | 25864         | 386.64          | 8                 | 25837         | 387.04          |                      |               |                 |
| 16.....                | 2                  | 25880         | 386.40          |                   |               |                 |                      |               |                 |
| 17.....                | 5                  | 25940         | 385.51          | 9                 | 25941         | 385.49          | 5                    | 25920         | 385.8           |
| 18.....                | 2                  | 26008         | 384.50          |                   |               |                 |                      |               |                 |
| 19.....                | 3                  | 26046         | 383.94          | 10                | 26044         | 383.97          | 6                    | 26080         | 383.4           |
| 20.....                | 2                  | 26066         | 383.64          |                   |               |                 |                      |               |                 |
| 21.....                | 2                  | 26090         | 383.28          |                   |               |                 |                      |               |                 |
| 22.....                | 2                  | 26123         | 382.80          |                   |               |                 |                      |               |                 |
| 23.....                | 3                  | 26161         | 382.25          | 11                | 26168         | 382.15          |                      |               |                 |
| 24.....                | 4                  | 26196         | 381.74          |                   |               |                 |                      |               |                 |
| 25.....                | 4                  | 26256         | 380.87          |                   |               |                 |                      |               |                 |
| 26.....                | 5                  | 26295         | 380.30          | 12                | 26300         | 380.23          | 7                    | 26280         | 380.5           |
| 27.....                | 4                  | 26325         | 379.87          |                   |               |                 |                      |               |                 |
| 27 $\frac{1}{2}$ ..... | 1                  | 26385         | 379.00          |                   |               |                 |                      |               |                 |
| 28.....                | 2                  | 26411         | 378.63          |                   |               |                 |                      |               |                 |
| 29.....                | 3                  | 26448         | 378.10          | 13                | 26445         | 378.14          |                      |               |                 |
| 30.....                | 3                  | 26515         | 377.15          | 14                | 26528         | 376.96          |                      |               |                 |
|                        |                    |               |                 |                   |               |                 |                      |               |                 |
| 31.....                | 2                  | 26547         | 376.69          |                   |               |                 |                      |               |                 |
| 32.....                | 3                  | 26590         | 376.08          |                   |               |                 |                      |               |                 |
| 33.....                | 2                  | 26610         | 375.80          |                   |               |                 |                      |               |                 |
| 34.....                | 5                  | 26645         | 375.30          |                   |               |                 |                      |               |                 |
| 35.....                | 5                  | 26661         | 375.08          | 15                | 26663         | 375.05          |                      |               |                 |
| 36.....                | 5                  | 26696         | 374.59          |                   |               |                 |                      |               |                 |
| 37.....                | 3                  | 26720         | 374.25          |                   |               |                 | 8                    | 26730         | 374.1           |
| 38.....                | 5                  | 26760         | 373.69          | 16                | 26765         | 373.62          |                      |               |                 |
| 39.....                | 4                  | 26783         | 373.37          |                   |               |                 |                      |               |                 |
| 40.....                | 3                  | 26827         | 372.76          |                   |               |                 |                      |               |                 |
|                        |                    |               |                 | 17                | 26837         | 372.62          |                      |               |                 |
| 41.....                | 3                  | 26853         | 372.40          |                   |               |                 |                      |               |                 |
| 42.....                | 2                  | 26880         | 372.02          |                   |               |                 |                      |               |                 |

WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS  
 OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM—*Continued*
REGION OF 2.6  $\mu$ —*Continued*

| 15,000-LINE GRATING |                    |               |                 | 7500-LINE GRATING |               |                 | HILGER BRASS GRATING |               |                 |
|---------------------|--------------------|---------------|-----------------|-------------------|---------------|-----------------|----------------------|---------------|-----------------|
| Band No.            | Relative Intensity | Wave-Length A | Wave No. per mm | Band No.          | Wave-Length A | Wave No. per mm | Band No.             | Wave-Length A | Wave No. per mm |
| 43.....             | 4                  | 26930         | 371.33          | 18                | 26936         | 371.25          |                      |               |                 |
| 44.....             | 1                  | 26974         | 370.73          |                   |               |                 |                      |               |                 |
| 45.....             | 3                  | 27006         | 370.29          | 19                | 27002         | 370.34          |                      |               |                 |
| 46.....             | 1                  | 27044         | 369.77          |                   |               |                 |                      |               |                 |
| 47.....             | 4                  | 27084         | 369.22          | 20                | 27093         | 369.10          |                      |               |                 |
| 48.....             | 4                  | 27103         | 368.96          |                   |               |                 |                      |               |                 |
| 49.....             | 3                  | 27168         | 368.08          |                   |               |                 |                      |               |                 |
| 50.....             | 5                  | 27198         | 367.67          | 21                | 27193         | 367.74          | 9                    | 27180         | 367.9           |
| 51.....             | 5                  | 27236         | 367.15          |                   |               |                 |                      |               |                 |
| 52.....             | 1                  | 27278         | 366.60          |                   |               |                 |                      |               |                 |
| 53.....             | 1                  | 27294         | 366.38          |                   |               |                 |                      |               |                 |
| 54.....             | 1                  | 27314         | 366.11          |                   |               |                 |                      |               |                 |
| 55.....             | 3                  | 27340         | 365.76          |                   |               |                 |                      |               |                 |
| 56.....             | 5                  | 27386         | 365.15          | 22                | 27395         | 365.03          |                      |               |                 |
| 57.....             | 5                  | 27407         | 364.87          |                   |               |                 | 10                   | 27430         | 364.6           |
| 58.....             | 2                  | 27445         | 364.37          |                   |               |                 |                      |               |                 |
| 59.....             | 2                  | 27479         | 363.91          |                   |               |                 |                      |               |                 |
| 60.....             | 2                  | 27511         | 363.49          |                   |               |                 |                      |               |                 |
| 61.....             | 5                  | 27545         | 363.04          | 23                | 27544         | 363.06          |                      |               |                 |
| 62.....             | 4                  | 27614         | 362.14          |                   |               |                 |                      |               |                 |
| 63.....             | 3                  | 27625         | 361.99          | 24                | 27623         | 362.02          | 11                   | 27620         | 362.0           |
| 64.....             | 3                  | 27655         | 361.60          |                   |               |                 |                      |               |                 |
| 65.....             | 3                  | 27668         | 361.43          |                   |               |                 |                      |               |                 |
| 66.....             | 3                  | 27700         | 361.01          |                   |               |                 |                      |               |                 |
| 67.....             | 3                  | 27712         | 360.85          |                   |               |                 |                      |               |                 |
| 68.....             | 2                  | 27765         | 360.17          |                   |               |                 |                      |               |                 |
| 69.....             | 2                  | 27777         | 360.01          | 25                | 27784         | 359.92          |                      |               |                 |
| 70.....             | 2                  | 27803         | 359.67          |                   |               |                 |                      |               |                 |
| 71.....             | 2                  | 27819         | 359.47          |                   |               |                 |                      |               |                 |
| 72.....             | 3                  | 27867         | 358.85          | 26                | 27866         | 358.86          |                      |               |                 |
| 73.....             | 1                  | 27926         | 358.09          |                   |               |                 |                      |               |                 |
| 74.....             | 1                  | 27947         | 357.82          |                   |               |                 |                      |               |                 |
| 75.....             | 1                  | 27972         | 357.50          |                   |               |                 |                      |               |                 |
| 76.....             | 4                  | 28029         | 356.77          | 27                | 28031         | 356.75          | 12                   | 28030         | 356.8           |
| 77.....             | 2                  | 28077         | 356.16          |                   |               |                 |                      |               |                 |
| 78.....             | 1                  | 28103         | 355.83          |                   |               |                 |                      |               |                 |
| 79.....             | 2                  | 28140         | 355.37          |                   |               |                 |                      |               |                 |
| 80.....             | 3                  | 28197         | 354.65          | 28                | 28198         | 354.64          |                      |               |                 |
| 81.....             | 2                  | 28267         | 353.77          |                   |               |                 |                      |               |                 |
| 82.....             | 2                  | 28336         | 352.91          | 29                | 28348         | 352.76          | 13                   | 28350         | 352.7           |
| 83.....             | 2                  | 28373         | 352.45          |                   |               |                 |                      |               |                 |
| 84.....             | 2                  | 28485         | 351.06          |                   |               |                 |                      |               |                 |
| 85.....             | 2                  | 28538         | 350.41          | 30                | 28540         | 350.38          | 14                   | 28540         | 350.4           |
| 86.....             | 1                  | 28590         | 349.77          |                   |               |                 |                      |               |                 |
| 87.....             | 1                  | 28658         | 348.94          | 31                | 28710         | 348.31          |                      |               |                 |
|                     |                    |               |                 |                   |               |                 | 15                   | 28990         | 344.9           |
|                     |                    |               |                 |                   |               |                 | 16                   | 29210         | 342.4           |
|                     |                    |               |                 |                   |               |                 | 17                   | 29750         | 336.1           |



WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS  
OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM—*Continued*PART OF THE REGION OF  $6\mu$ 

Hilger brass grating

| Band No. | Wave-Length<br>A | Wave No.<br>per mm | Distance from<br>Center, $159.6$ | Mean Distance<br>of One Pair |
|----------|------------------|--------------------|----------------------------------|------------------------------|
| 1.....   | 50220            | 199.1              | 39.5                             |                              |
| 2.....   | 50850            | 196.7              | 37.1                             |                              |
| 3.....   | 51110            | 195.7              | 36.1                             |                              |
| 4.....   | 51490            | 194.2              | 34.6                             |                              |
| 5.....   | 51720            | 193.4              | 33.8                             |                              |
| 6.....   | 52040            | 192.2              | 32.6                             |                              |
| 7.....   | 52420            | 190.8              | 31.2                             |                              |
| 7'.....  | 52600            | 190.1              | 30.5                             |                              |
| 8.....   | 52800            | 189.4              | 29.8                             |                              |
| 9.....   | 52960            | 188.8              | 29.2                             |                              |
| 9'.....  | 53090            | 188.4              | 28.8                             |                              |
| 10.....  | 53520            | 186.8              | 27.2                             |                              |
| 11.....  | 54240            | 184.4              | 24.8                             |                              |
| 11'..... | 54470            | 183.6              | 24.0                             |                              |
| 12.....  | 54660            | 182.9              | 23.3                             |                              |
| 13.....  | 55250            | 181.0              | 21.4                             |                              |
| 13'..... | 55570            | 179.9              | 20.3                             |                              |
| 14.....  | 55810            | 179.2              | 19.6                             |                              |
| 15.....  | 56170            | 178.0              | 18.4                             |                              |
| 16.....  | 56430            | 177.2              | 17.6                             |                              |
| 17.....  | 56800            | 176.1              | 16.5                             |                              |
| 17'..... | 56920            | 175.7              | 16.1                             |                              |
| 18.....  | 57170            | 174.9              | 15.3                             |                              |
| 18'..... | 57470            | 174.0              | 14.4                             |                              |
| 19.....  | 57680            | 173.4              | 13.8                             |                              |
| 20.....  | 58240            | 171.7              | 12.1                             | 12.2                         |
| 20'..... | 58640            | 170.5              | 10.9                             | 10.8                         |
| 21.....  | 58830            | 170.0              | 10.4                             |                              |
| 21'..... | 58950            | 169.6              | 10.0                             | 9.9                          |
| 22.....  | 59380            | 168.4              | 8.8                              | 8.8                          |
| 22'..... | 59720            | 167.5              | 7.9                              | 7.9                          |
| 23.....  | 59880            | 167.0              | 7.4                              | 7.4                          |
| 24.....  | 60160            | 166.2              | 6.6                              | 6.4                          |
| 25.....  | 60480            | 165.3              | 5.7                              | 5.6                          |
| 26.....  | 60720            | 164.7              | 5.1                              |                              |
| 27.....  | 61140            | 163.6              | 4.0                              | 3.9                          |
| 27'..... | 61440            | 162.8              | 3.2                              | 3.2                          |
| 28.....  | 61620            | 162.3              | 2.7                              | 2.7                          |
| 29.....  | 61880            | 161.6              | 2.0                              | 2.0                          |
| 30.....  | 62160            | 160.9              |                                  |                              |
| 30'..... | 62420            | 160.2              |                                  |                              |
| 31.....  | 62720            | 159.4              |                                  |                              |
| 31'..... | 62890            | 159.0              |                                  |                              |
| 32.....  | 63440            | 157.6              | 2.0                              |                              |
| 33.....  | 63740            | 156.9              | 2.7                              |                              |
| 33'..... | 63930            | 156.4              | 3.2                              |                              |
| 34.....  | 64180            | 155.8              | 3.8                              |                              |
| 35.....  | 64530            | 155.0              | 4.6                              |                              |
| 36.....  | 64950            | 154.0              | 5.6                              |                              |
| 37.....  | 65200            | 153.4              | 6.2                              |                              |
| 38.....  | 65510            | 152.6              | 7.0                              |                              |

WAVE-LENGTHS AND WAVE-NUMBERS OF THE ABSORPTION BANDS  
 OF WATER-VAPOR IN THE NEAR INFRA-RED SPECTRUM—*Continued*
PART OF THE REGION OF  $6\mu$ —*Concluded*

Hilger brass grating

| Band No. | Wave-Length<br>$\text{\AA}$ | Wave No.<br>per mm | Distance from<br>Center, $159.6$ | Mean Distance<br>of One Pair |
|----------|-----------------------------|--------------------|----------------------------------|------------------------------|
| 39.....  | 65730                       | 152.1              | 7.4                              |                              |
| 40.....  | 65940                       | 151.7              | 7.9                              |                              |
| 41.....  | 66340                       | 150.7              | 8.9                              |                              |
| 42.....  | 66810                       | 149.7              | 9.9                              |                              |
| 43.....  | 67160                       | 148.9              | 10.7                             |                              |
| 44.....  | 67520                       | 148.1              | 11.5                             |                              |
| 45.....  | 67920                       | 147.2              | 12.4                             |                              |
| 46.....  | 68280                       | 146.5              | 13.1                             |                              |

## V. QUESTIONS OF INTERPRETATION

In addition to her work with water-vapor mentioned above, Eva von Bahr<sup>1</sup> has studied the absorption of HCl in the neighborhood of  $3.5\mu$ . The combination principle, with the quantum distribution of rotation-frequencies, has been applied by Bjerrum<sup>2</sup> to set forth reasons for the presence of these absorption bands of HCl and to calculate directly the size of energy quanta. However, the chaotic arrangement of water bands in the region of  $2.6\mu$ , as they appear in Fig. 5, does not appear to satisfy the demands of these hypotheses, though the region has in a general way a center and a rough appearance of symmetry. Since this work was completed Mr. E. H. Imes has mapped the absorption of HCl at  $3.5\mu$  with the apparatus here described, using an interval of about  $30\text{ \AA}$  in the slit of the thermopile. The wave-lengths are precisely determined by the grating, and a parabolic shift of the vibration-frequency with increasing rotation-frequency is very definitely displayed. Work on HCl showing this effect has been published by Kemble and Brinsmade,<sup>3</sup> though that done here was completed before their work appeared. The curve of Fig. 5 does show a crowding together of bands in the nearer end, which our experience with HCl would lead us at least to consider possible. But the uncertainty, due to

<sup>1</sup> *Verhandlungen der deutschen Physikalischen Gesellschaft*, **15**, 1150, 1913.

<sup>2</sup> *Ibid.*, **16**, 614, 1914.

<sup>3</sup> *Proceedings of the National Academy of Sciences*, **3**, 420, 1917.

the general complexity of the curve, as to which band should be associated with any other to make a pair, and about the location of the vibration center for no rotation, has so far deferred our explanation. The third rotation series mentioned in connection with the work of Rubens and Hettner may perhaps be appealed to as a probable cause of the complexity both at  $2.6$  and  $6\ \mu$ .

The appearance of the curves, particularly of Fig. 5, suggests that useful knowledge may be still further advanced by an increase in dispersion. In the case of the  $2.6\ \mu$  region, however, neither a finer nor a larger grating would serve this purpose; but a source of greater energy, or a more sensitive detector, would enable us to use narrower slits. We hope to profit by the use of a tungsten ribbon lamp in place of the glower. We may be able to build another more sensitive galvanometer.

It should be pointed out that the selective atmospheric absorption near  $2.6$  and  $6\ \mu$  may account for the unexpected weakness or even the non-appearance of bright lines predicted by the laws of series in the spectra of elements.

It is hoped to employ the apparatus in the further study of absorption, and it may be that the behavior of carbon dioxide will help to explain that of water-vapor. The work here described was undertaken at the suggestion of Professor H. M. Randall, to whom the author makes grateful acknowledgment of his indebtedness.

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